

Facile Synthesis and Colloidal Stabilization of Metal Nanoparticles in Aqueous Amphiphilic Block Copolymer Solutions

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The development of simple and versatile methods for the preparation of nanoparticles in a size or shape-selected and –controlled manner is an important and challenging task.^{1,2} In addition, utilization of non-toxic chemicals, environmentally benign solvents, and renewable materials are emerging issues that merit important consideration in a synthetic strategy.³

We present here the facile synthesis and effective stabilization of gold nanoparticles through autoreduction of hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) in aqueous poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) amphiphilic block copolymer solutions at ambient conditions.⁴ Gold nanoparticles were prepared by simply mixing an aqueous $2 \times 10^{-3} \text{ mol L}^{-1}$ $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution with an aqueous homopolymer PEO (PEG6000, $(\text{EO})_{136}$) solution or an aqueous PEO-PPO-PEO block copolymer (Pluronic P103, $(\text{EO})_{17}(\text{PO})_{60}(\text{EO})_{17}$, or Pluronic F127, $(\text{EO})_{100}(\text{PO})_{65}(\text{EO})_{100}$, BASF Corp.) solution so that the final AuCl_4^- concentration was $2 \times 10^{-4} \text{ mol L}^{-1}$.

The reduction of AuCl_4^- and the formation of gold nanoparticles were monitored by observing changes in the absorption spectra centered at $\sim 220 \text{ nm}$ for the gold(III) chloride solutions⁵ and those centered at $\sim 540 \text{ nm}$ originating from the surface plasmon of the gold nanoparticles⁶. **Figure 1** shows absorbance spectra obtained at 2 hours after mixing an aqueous AuCl_4^- ion solution and a 5.0 mM aqueous Pluronic P103 or Pluronic F127 block copolymer solution. Also shown for comparison purposes are absorbance spectra recorded at 2 hours and at 2 days after mixing an aqueous AuCl_4^- ion solution and a 5.0 mM aqueous PEO

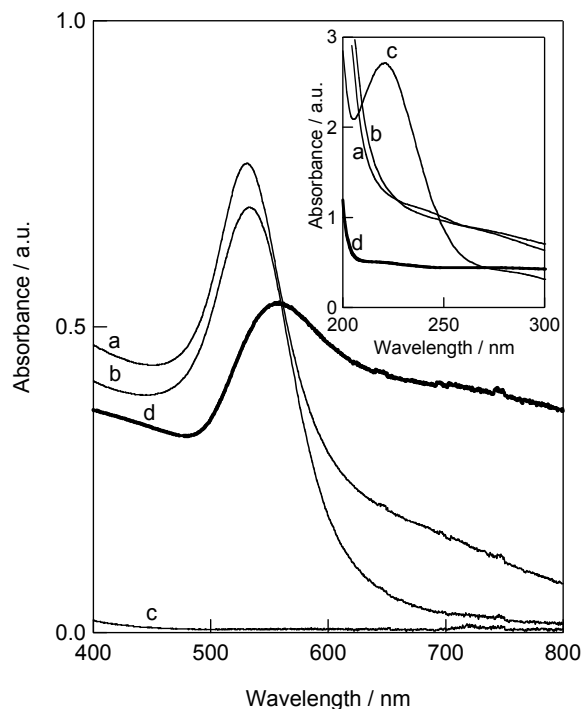


Figure 1. Absorption spectra recorded at 2 hours after mixing an aqueous AuCl_4^- ion solution and a 5.0 mM aqueous (a) Pluronic P103 or (b) Pluronic F127 block copolymer solution. Also shown for comparison are absorbance spectra at (c) 2 hours and (d) 2 days after mixing an aqueous AuCl_4^- ion solution and a 5.0 mM aqueous PEO

homopolymer solution (the PEO molecular weight was selected to be intermediate to that of Pluronic P103 and Pluronic F127). At 2 hours after initiating the reaction, the absorption band centered at ~540 nm (due to gold nanoparticles) was prominent in both Pluronic P103 and Pluronic F127-containing solutions but was not observed at all in the PEO homopolymer solution. Correspondingly, the absorption band centered at 220 nm (due to AuCl_4^- ions) was pronounced after 2 hours in the aqueous PEO homopolymer solution but not in the case of aqueous Pluronic P103 and F127 block copolymer solutions. It took ~2 days for gold nanoparticles to form in the PEO homopolymer-containing system.

It is notable that the gold nanoparticles thus produced in aqueous PEO-PPO-PEO block copolymer solutions are highly stable even at low polymer concentration (molar ratio of AuCl_4^- /block copolymer = ~1/10) and show no signs of aggregation and precipitation even after 8 months left standing at ambient temperature. On the contrary, precipitation of gold nanoparticles occurred after only 2 days when we synthesized them using PEO homopolymer as reductant/stabilizer. The colloidal stabilization of gold nanoparticles by PEO-PPO-PEO block copolymers is most likely due to their amphiphilic character and their ability to form micelles in solution and/or on the surface of particles.⁷ It becomes evident from the above that amphiphilic PEO-PPO-PEO block copolymers confer a distinct advantage over PEO homopolymer both as reaction media and as stabilizers.

The effect of polymer concentration on the AuCl_4^- ion reduction and nanoparticle formation is shown in **Figure 2**. At 2 hours after the initiation of the reaction, the absorption centered at 240 nm (due to AuCl_4^- ions) was high and independent of PEO homopolymer concentration, while the absorbance decreased with an increase in Pluronic P103 or F127 block copolymer concentration, gradually until 1.0 mM, and then more abruptly. The absorbance at

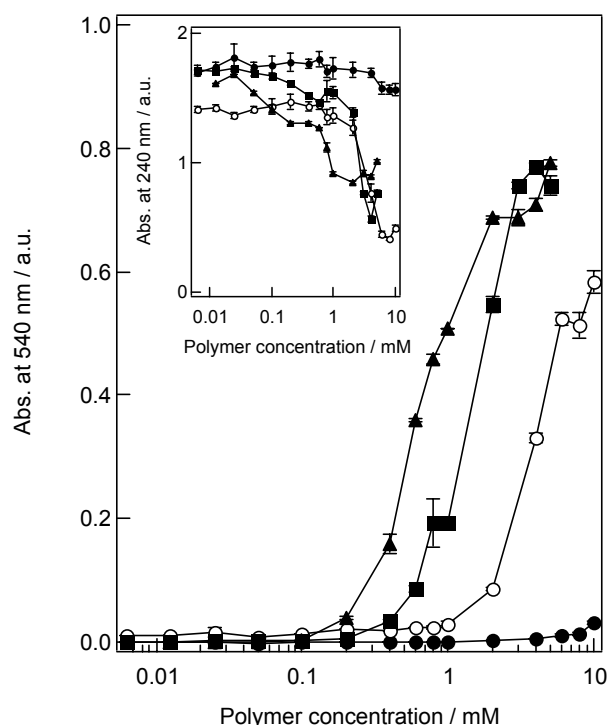


Figure 2. Absorbance at ~540 nm at 2 hours after mixing aqueous AuCl_4^- ion solution and aqueous Pluronic P103 (■) or Pluronic F127 (▲) block copolymer solutions, plotted as a function of polymer concentration. Also shown are absorbances at ~540 nm at 2 hours (●) and 2 days (○) after mixing aqueous AuCl_4^- ion solutions and aqueous PEO homopolymer solutions. The insert shows absorbances at 240 nm for the same systems and conditions.

~540 nm (due to gold nanoparticles) started to increase from ~0.1 mM Pluronic, while a small increase of absorbance at ~540 nm was observed only above 6.0 mM PEO after 2 hours. At ~2 days after mixing, the absorbances at 240 nm decreased compared to those recorded at 2 hours. The absorbance of the PEO system at 240 nm decreased drastically above ~2.0 mM PEO; correspondingly, the absorbance at ~540 nm increased.

The size and shape of the obtained gold nanoparticles were determined by TEM (see **Figure 3**). Spherical nanoparticles with number average diameters of 8.3 nm (standard deviation 4.8 nm) and 11.3 nm (standard deviation 10.0 nm) were observed in aqueous Pluronic P103 and F127 solutions, respectively.

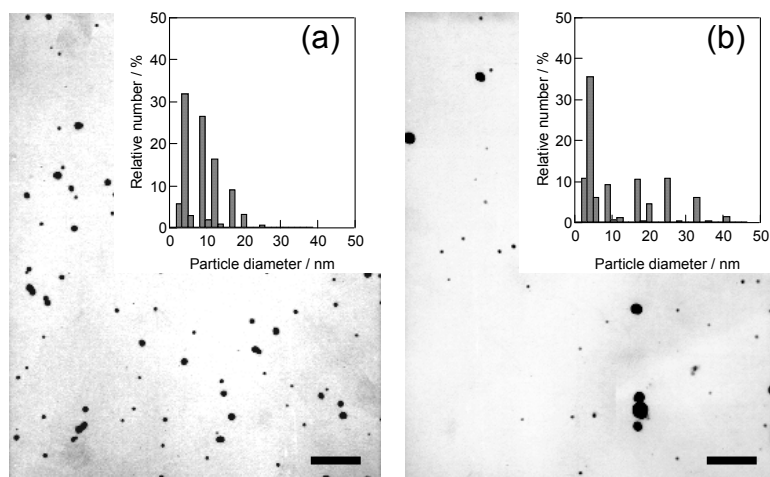


Figure 3. Electron micrographs and size distributions of gold nanoparticles produced in (a) Pluronic P103 and (b) Pluronic F127 block copolymer solutions. The Pluronic concentration is 1.0 mM. The scale bar represents 100 nm.

The observations what we report here suggest that the formation of gold nanoparticles from HAuCl_4

comprises three main steps: (1) reduction of metal ions by block copolymer, (2) absorption of block copolymer on gold atoms and/or clusters and reduction of metal ions on the surface of

gold atoms and/or clusters, and (3) growth of metal particles and stabilization by block copolymers (**Figure 4**). This mechanism is consistent with the observed increase of reaction activity with increase in the molecular weight, PEO block length and/or concentration (see

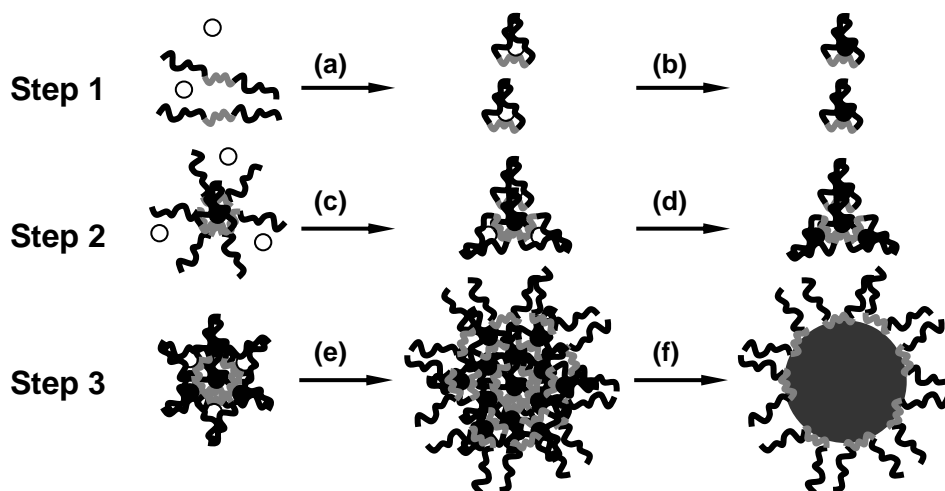


Figure 4. Proposed mechanism of AuCl_4^- reduction and particle formation: (○) AuCl_4^- and (●) Au. Step 1: (a) pseudocrown ether cavity complexing AuCl_4^- and (b) AuCl_4^- reduction. Step 2: (c) polymer adsorption on Au, cavity formation and (d) AuCl_4^- reduction. Step 3: (e) further growth and (f) stabilization.

Figure 2) of the block copolymer. The contribution of PPO is manifested in the much higher reaction activity of PEO-PPO-PEO block copolymers compared to that of PEO homopolymer

(see **Figures 1 and 2**).

In conclusion, the synthesis of gold nanoparticles with diameter of ~10 nm has been achieved at ambient conditions by simply mixing an aqueous hydrogen tetrachloroaurate (III) hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) solution with an aqueous amphiphilic PEO-PPO-PEO block copolymer solution.⁴ The block copolymer molecular weight and PEO and PPO block lengths controlled the reaction activity of the block copolymer with AuCl_4^- ions. The higher efficiency of particle formation in block copolymer systems compared to PEO homopolymer system is caused by the contributions of the adsorption and the growth processes (steps 2 and 3 in **Figure 4**). The size of gold nanoparticles produced was determined by a competition between reaction activity and adsorption of block copolymer. Higher reaction activity with AuCl_4^- ions of PEO-PPO-PEO block copolymers having higher PEO content (PEO block length) leads to a size increase. PPO blocks contribute to block copolymer adsorption on gold atoms, clusters and/or particles after reduction of AuCl_4^- ions, so that particle growth seems to be prevented, and smaller particles and higher colloidal stability result.

The synthesis method presented here is environmentally benign since it involves water and polymers that are not only non-toxic but also approved for pharmaceutical use.⁸ It is also economical as it proceeds fast to completion and results in a “ready-to-use” product. Moreover, variation of the block copolymer molecular characteristics and the relative concentration of the reactants allows for tunability of particle properties.

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